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PIXE facility for trace element analysis at IGCAR, Kalpakkam, India

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Abstract : A Proton Induced X-ray Emission (PIXE) System has been designed and developed with all the necessary instrumentation in one of the beam lines of the 2 MV Tandem accelerator at the Materials Science Division, Indira Gandhi Centre for Atomic Research (IGCAR) Kalpakkam, India for measuring trace element levels in a variety of samples. The system has been calibrated using standard solutions The linearity and sensitivity were studied using 1 MeV proton beam Using the PIXE system, trace element analysis of standard water samples from NIST (National Institute of Standards and Technology, USA) and water samples from the river Chaliyar has been carried out This paper describes the experimental arrangement and details about the calibration and presents some of the results.

Keywords : PIXE accelerators, trace elemental analysis, environmental applications

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1. Introduction

Characteristic X-ray emission follows the ionisation of an atom due to the rearrangement of electrons after ejection of a deeply bound electron. The ionisation can be induced by photons, electrons, protons, alpha particles or by other heavy ions. Proton induced X-ray emission (PIXE) is well suited because of the very low bremsstrahlung background, better signal to noise ratio and high X-ray production cross section [1]. It has been successfully used by various groups all over the world for trace element analysis in a variety of research fields—biology, environment, archaeology, medicine and forensic science. PIXE is similar to other forms of X-ray emission techniques like X-ray fluorescence (XRF) and Electron probe microanalysis (EPMA). The difference in only is the method of excitation.

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The major advantages of PIXE are its multielemental character, its high sensitivity (absolute detection limits down to 10^{-12} g and relative detection limits down to 0.1 μg/g), speed of analysis (1–10 mins), non-destructive nature and ability to analyse tiny samples (less than 1 mg). To make use of the above advantages of the technique, appropriate experimental arrangements and procedures have to be developed. It is therefore essential that careful attention is given to all the stages of PIXE experimental arrangements. Several international conferences on PIXE and its analytical applications [2–6] have clearly demonstrated the development and uses of PIXE technique. In the last few years, a few PIXE set-ups [7–9] have brought out improved versions of their earlier experimental arrangements

The present work describes the experimental set-up designed and fabricated for routine analysis of trace elements in a variety of samples. The set-up has been installed in one of the beam lines of the indigenously developed 2 MV Tandem accelerator at the Materials Science Division, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India. Calibration of the system with standard samples normally used for Atomic absorption spectroscopy (AAS) and NIST standard water samples has been discussed. The details of the trace element analysis of river water samples carried out using this system are also discussed.

2. Experimental arrangement

The schematic diagram of the PIXE facility is shown in Figure 1. The PIXE chamber has multiple ports to accommodate the Si(Li) detector for the detection of X-rays and Silicon Surface Barrier (SSB) detector for the detection of backscattered particles, beam viewer,

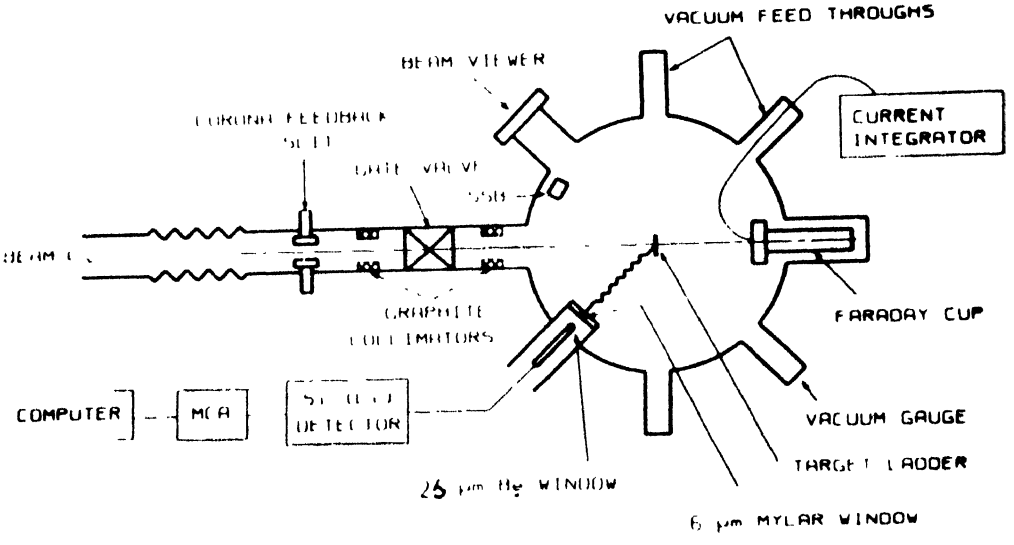

Figure 1. A schematic diagram of the PIXE experimental arrangement

faraday cup for beam current measurements, vacuum feedthroughs and vacuum gauges. The top flange accommodates a ladder arrangement for target mounting. The ladder can be

raised or lowered for beam alignment. A Wilson seal arrangement has been provided for moving the ladder without disturbing the vacuum in the chamber. A rectangular sample holder made of aluminium with a series of circular holes of diameter 10 mm each in the centre, has been fabricated for mounting the samples. A 8 mm diameter, 6 μm thick mylar window has been provided in the 135° port inside the chamber facing the Si(Li) detector, in order to protect the detector from the formation of surface layers caused by sputtering and evaporation of material from the bombarded samples. The target ladder in the top flange of the scattering chamber is electrically insulated from the beam line and is connected to the faraday cup, so that the charge accumulated on the sample can be collected by a current integrator. The chamber is maintained at a pressure in the range of 10^{-5} – 10^{-6} mbar. Two graphite collimators of 4 mm diameter each are put in the entrance port to collimate the beam. A retractable Lithium drifted Silicon (Si(Li)) detector is inserted in the chamber at 135° relative to the incident ion beam for X-ray detection. The Si(Li) detector has an active area of 30 mm^2 and a resolution of 160 eV at 5.9 keV (FWHM).

The 2 MV tandem accelerator at the Materials Science Division, IGCAR, Kalpakkam, has been used for our PIXE studies. The details about the accelerator are described elsewhere [10]. The beam emerging from the accelerator passes through a bending magnet with a field stability of 100 ppm. In order to achieve energy stability, the beam is made to pass through a slit assembly. The current picked up by the plates of the slit is used in a feed back mode as an error signal, to correct the terminal voltage of the accelerator, which decides the energy stability. The beam is collimated by two graphite collimators before it falls on the sample. The beam then enters the target holder which has a provision for mounting a number of samples. The ion induced X-rays from the sample pass through a 6 μm thick mylar window and a 25 μm Be window before reaching the Si(Li) detector. The spectrum is analysed and recorded in the multichannel analyser. AXIL software [11] has been used for the data analysis.

3. Calibration of the PIXE system

Calibration is one of the most important procedures in the PIXE analysis. The calibration of the PIXE set-up can be carried out in two ways : (a) based fully on experimental procedures. *i.e.* sensitivity factors normally expressed in units of counts/μg cm^{-2}.μC are determined from the measurements performed on the standard samples which are made of pure elements or chemical compounds [12]. (b) deduced theoretically or in a semiemperical way from the calculated cross sections of X-ray excitation and from the absorption data with the absorber foil present between the target and the detector. We have followed the first approach using standard samples for our PIXE system as it gives a better accuracy. Thin and uniform samples are required as standard samples for the PIXE analysis.

Standard samples were prepared from the standard solutions normally used for the AAS analysis. Single element standard solutions (1000 ppm) of S, Cl, K, Ca, Mn, Ni, Cu, Zn and Pd for K X-rays and Pb, Hg, Ta, W and Bi for L X-rays have been taken for our calibration study. One drop having a volume of 200 μl of each solution was taken using

the micropipet and dropped onto the 5 μm thick Aluminised mylar film and dried using an IR lamp.

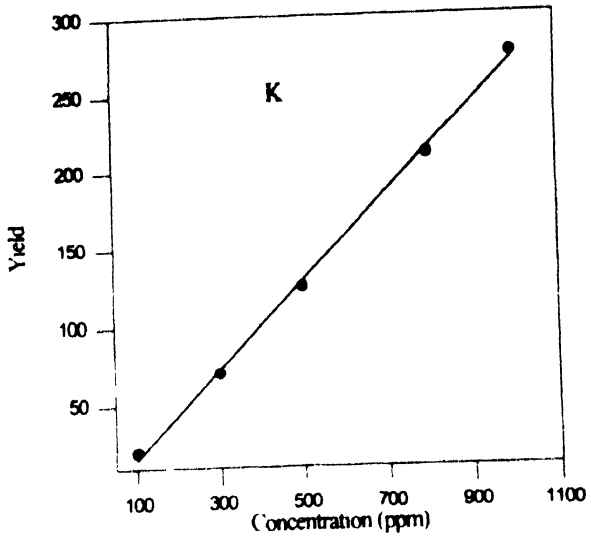

Figure 2. The linearity curve for the element K.

3.1. Linearity of yield :

To test the linearity of the X-ray yield at various sample concentrations, standard samples of K, Ca, Pd and Pb of concentrations from 100–1000 ppm were prepared. Experiments were carried out using 1 MeV proton beam. The typical linearity curve for the element K is shown in Figure 2. It is seen that the X-ray yields at various concentrations are linear. The above experiments were repeated several times for checking the consistency.

3.2. Sensitivity determination :

Experiments were carried out using 1 MeV proton beam on the multielement standard solutions of S, Cl, K, Ca, V, Cr, Fe, Ni, Cu, Zn, Mo, Pd, Ta, W, Pb, Hg and Bi. The samples were prepared as described earlier. The X-ray yield

$$I_z = Q\sigma_z(E_p)(Nt)_z \Delta\Omega\varepsilon T, \tag{1}$$

where I_z is the intensity of the element with atomic number Z, Q is the charge *i.e.* number of protons incident on the target, $\sigma_z(E_p)$ is the X-ray production cross section with energy E_p, $(Nt)_z$ is the number of atoms per unit area, $\Delta\Omega$ is the solid angle subtended by the Si(Li) detector, ε is the efficiency of the detector and T is the transmission of X-rays with a given energy through the absorbing material between the target and the detector. From eq. (1) we can write $I_z = K_z Q(Nt)_z$,

from which $K_z = I_z / Q(Nt)_z$. (2)

The target sensitivity K_z is determined by measuring the K and L X-ray yields/μg cm^{-2}.μC. The sensitivity curves of K and L X-rays used in this study are shown in Figure 3.

If all the parameters of eq. (1) is measured, the concentration of any element can be obtained without using internal standard. Using the internal standard intensity, one can

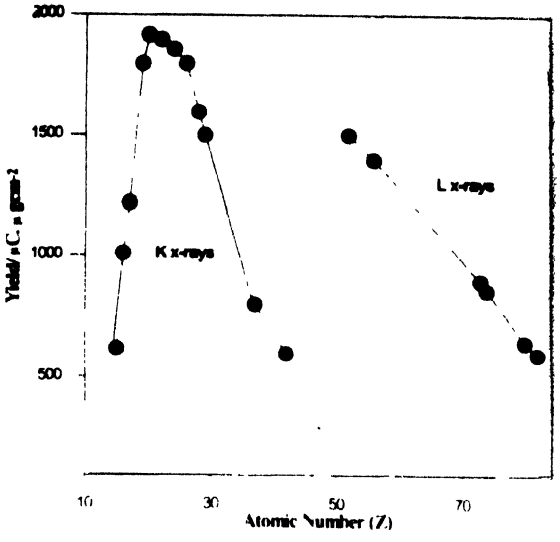

Figure 3. Sensitivity curve of K_α and L_α X-ray yield as a function of atomic number for our PIXE system

estimate the elemental concentrations as follows. The target sensitivity K_z is actually the product of $\sigma(E_p)$, $\Delta\Omega$, ε and T. From eq. (2), one can write for internal standard

$$K_s = I_s / Q(Nt)_s. \tag{3}$$

If x is the respective elemental concentration to be estimated then eq. (2) becomes

$$K_x = I_x / Q(Nt)_x. \tag{4}$$

From eqs. (3) and (4), we can get the value of K_s/K_x for each element

Pd has been used as the internal standard for trace element analysis in different samples. By taking into account the Pd yield and concentration in the spectrum, one can estimate the unknown elemental concentration C_x using the following relation.

$$C_x = \frac{K_s I_x}{K_x I_s} C_s, \tag{5}$$

where C_s is the internal standard concentration, I_s is the intensity of the internal standard and I_x is the intensity of the respective element. The concentrations C_x and C_s are proportional to $(Nt)_x$ and $(Nt)_s$.

4. Trace element analysis

Trace element analysis has acquired a great significance in the estimation of pollutants in environment. PIXE has been used for the above analysis in the last few decades [13]. Trace element analysis of the standard reference materials and river water samples has been carried out and discussed here.

4.1. Analysis of the NIST water :

When validating an analytical system the complete procedure must be standardised using a reference material from an established agency like IAEA or NIST. It should be similar to the unknown samples, in terms of analytes, matrix and physical form. We have taken the NIST SRM 1643d water reference sample for analysis. Samples were deposited on aluminised mylar as described earlier. Experiments were carried out using 1 MeV proton beam from the accelerator. The typical spectrum of NIST SRM 1643d water sample is shown in Figure 4. All the elements present in the reference material are seen in the

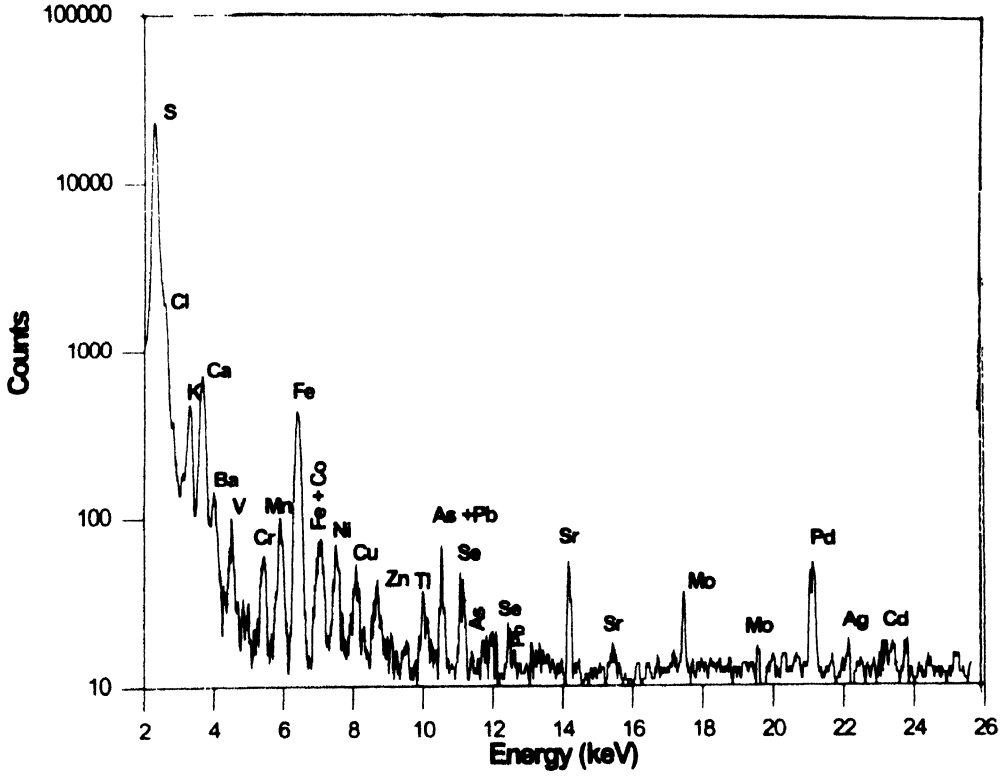

Figure 4. PIXE spectrum of NIST standard reference material SRM 1643d showing peaks of different elements

spectrum. Pd, used as an internal standard, is added to the sample for quantification. The experimental PIXE spectrum has been analysed by means of linear least square fitting procedure with the help of AXIL software [11], after subtracting the background contribution from the blank. In the AXIL software [11], the peak overlap (*e.g.* between AsK_α and PbL_α, where the separation of 8 eV is less than the natural line width AsK_α) could be dealt with in an exact manner, by making use of the known ratios of K_α/K_β and L_α/L_β of the lines of respective element. Using eq. (5), the trace elemental concentrations are estimated. The reproducibility has been checked by carrying out different runs on the sample. The values are tabulated in Table 1 along with the certified values. The typical

errors are indicated in the table. From the table, it can be seen that our measurements for most of the elements are in close agreement with the certified values. The elements Cr, Co,

Table 1. Trace element analysis of NIST SRM 1643d water samples.

Element	Certified values (ppb)	PIXE analysis results (ppb)
K	2356 ± 35	2250 ± 60
Ca	31040 ± 500	30842 ± 500
V	35 1 ± 1.4	32.4 ± 3.5
Cr	18.53 ± 0.20	15 8 ± 0.2
Mn	37.66 ± 0.83	35 ± 1.5
Fe	91 2 ± 3.9	95 ± 4 0
Co	25.00 ± 0.59	23 ± 2
Ni	58.1 ± 2.7	56 ± 2
Cu	20.5 ± 3.8	18 ± 3 2
Zn	72 48 ± 0.65	80 ± 2.0
As	56.02 ± 0.73	48 ± 1.95
Se	11.43 ± 0.17	9.8 ± 1.89
Mo	112.9 ± 1.7	105 ± 5.0
Ag	1.27 ± 0.057	0 8 ± 0.6
Cd	6.47 ± 0.37	5.2 ± 0.6
Ba	506.5 ± 8.9	500 ± 22
Tl	7.28 ± 0 25	6.5 ± 0.40
Sr	294.8 ± 3.4	270 ± 15.0
Pb	18 15 ± 0 64	16 ± 2

Cu, Se and Sr have a deviation of around 10–15% over the certified values. The deviation mainly arises from the overlapping peaks of adjacent elements.

4.2. Analysis of river water samples :

Drinking water is a significant source of essential elements of man and animals. Most of the water for drinking purposes is taken from the rivers. Water samples were collected from one of the rivers, Chaliyar, Kerala, India which is a major drinking water source for the local population. The river is heavily polluted by the industries situated along the river-bed, domestic wastes and agricultural wastes. Samples were prepared by dropping 200 µl of the water sample along with an internal standard Pd (2 ppm), onto 5 µm aluminised mylar foils. The samples were irradiated by 1 MeV proton beam from the 2 MV tandem accelerator. At the target, the beam current is kept around 5 nA to reduce dead time corrections and pile-up. The typical spectrum obtained from the river water sample is depicted in Figure 5. The K X-ray lines of P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Cu, Zn and Pd and L X-ray lines of Pb are detected. The spectrum has been analysed using AXIL software, after subtracting

the background contribution from the blank. By applying the intensity and concentration of the internal standard Pd in eq. (5), the elemental concentrations of all the elements present in the river water samples have been estimated and are listed in Figure 5. As can been seen

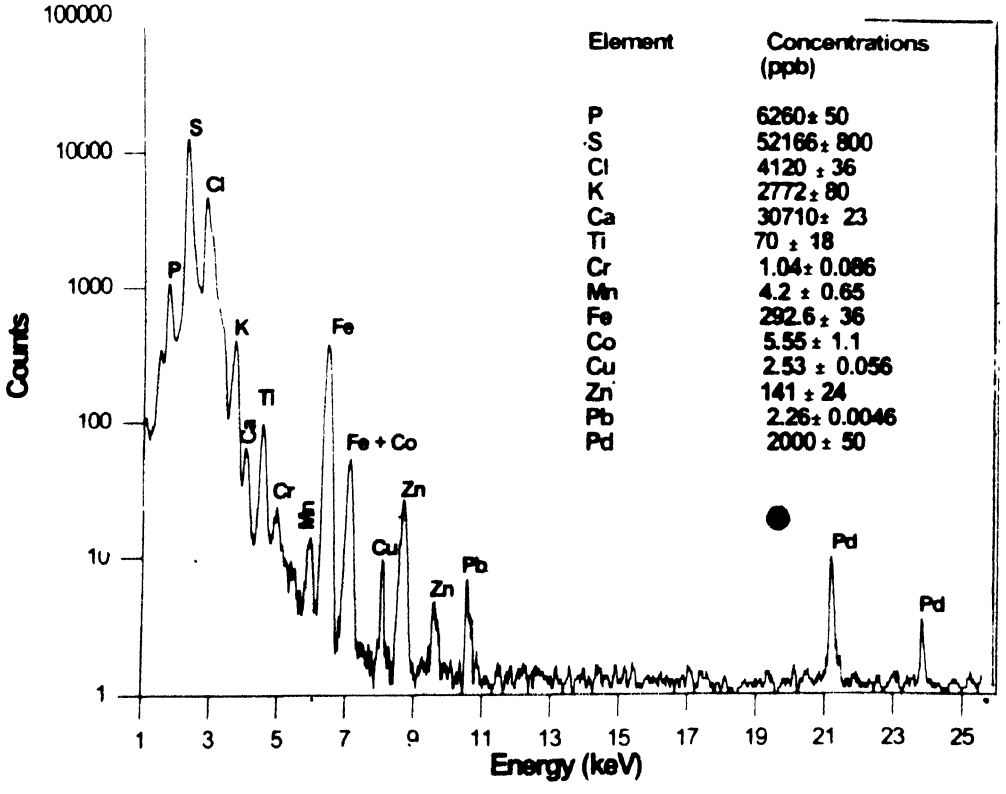

Figure 5. Typical spectrum of river water showing the elements with concentrations

from the figure, major elements P, S, Cl, K, Ca and Fe are present in the concentration level of 1000 ppb, the elements like Cr, Co, Cu and Pb are present in the level of 1–5 ppb. The Zn concentration is around 150 ppb. In general, our results are close to the Indian Standard Specifications for Drinking water [14].

4.3. Determination of minimum detection limit :

The minimum detection limit (MDL) for a given element may be defined as the minimum quantity of that element which must be present in the sample to yield a significant amount of signal above the noise to enable its identification and measurement. If the counts in the peak N_t due to trace elements exceeds three times the square root of the background N_b, taken within the FWHM of the peak, the peak may be observed, *i.e.* Nt > 3√ Nb. The background originating from ion interactions with matrix is independent of the presence of the trace element [15]. The minimum measurable concentration of trace element present, determined with the above criterion is shown in Figure 6. From the figure, we can see that

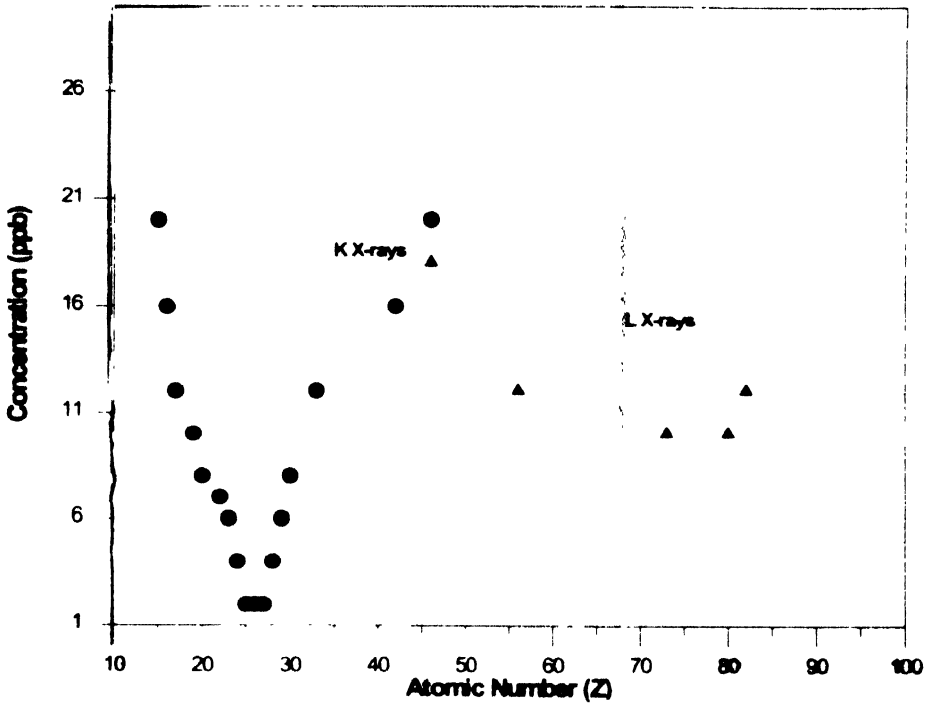

Figure 6. Calculated minimum concentration of trace elements detectable for protons on a thin target

the trace elemental concentrations in the region of $20 < Z < 30$ can be estimated up to 1 ppb level.

5. Summary

The PIXE experimental facility has been indigenously developed with the 2 MV tandem accelerator at the Materials Science Division, IGCAR, Kalpakkam for regular trace element analysis. The above facility has been calibrated following standard procedures. The facility is being utilised for finding out the trace elements in biological and environmental samples. Our results obtained with the NIST standard material has shown the reliability and accuracy of the system.

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